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Review of hydrogen-enriched gas production from steam gasification of biomass: The prospect of CaO-based chemical looping gasification

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ABSTRACT

Global warming, climate change and energy security issues are the forces driving the fossil fuel based energy system towards renewable and sustainable energy. Hydrogen as a clean energy carrier is believed to be the most promising source to replace fossil fuel. Biomass gasification with the presence of steam offers a feasible, sustainable, and environment-friendly option as well as a favorable alternative for higher hydrogen yields and for large-scale hydrogen production which can satisfy the need of hydrogen in the future. However, the process suffers from the problem of undesirable CO_2 and tar formation. Calcium oxide (CaO) has been acknowledged as a catalyst to produce hydrogen-rich gas and has currently gained broad attention due to its cheapness and abundance. Nevertheless, the deactivation of CaO after carbonation reaction is challenging for continuous hydrogen production and economical perspective. To conquer such challenge, the concept of CaO-based chemical looping gasification (CaO-based CLG) has emerged recently. Additionally, due to its energy-efficient and environment-friendly aspects, the CaO-based CLG using biomass as feedstock is gaining more attention in recent years. This study first presents a review on conventional steam gasification of biomass without catalysts for producing hydrogen-rich product gas. The effects of key variables, such as biomass characteristics, gasifier temperature, steam-to-biomass ratio (S/B) and equivalence ratio (ER), on hydrogen-enriched gas production are discussed based on recent researches and developments. Then the use of CaO in biomass steam gasification for hydrogen production with in situ CO_2 capture and tar reduction is described. The prospect of CaO-based CLG using biomass fuel is also discussed as a promising process for renewable, sustainable and environment-friendly hydrogen production.

Contents

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1. Introduction

Global warming, climate change and energy security have been gaining more attention worldwide. These are the major forces driving the dependence on fossil energy towards renewable and sustainable energy. Hydrogen as a clean energy carrier has been projected as the most promising source of energy that can be used in internal combustion engines as well as fuel cells with less pollution on the environment, especially without CO_2 emission [1–3]. Currently, there are a number of energy sources and technologies to produce hydrogen but about 99% of hydrogen comes from fossil fuels, mainly by steam reforming of natural gas which is the fossil fuel based process that could not address above serious concerns [4]. To meet the renewable and sustainable hydrogen production, biomass is considered as the ideal primary energy source for gradually replacing the depleting fossil fuels [5]. It is also accepted as the greatest promise due to its availability everywhere in the world [2].

Though hydrogen can be sustainably produced from biomass, the technologies for this are not yet fully developed [6]. The technologies available for biomass conversion into hydrogen-rich gas can be generally classified into biological and thermo-chemical routes [6–9]. Among them, the latter is concluded to be more economically viable and likely to become competitive with the conventional natural gas reforming method [10,11]. Gasification as one of the thermo-chemical processes is agreed to be favorable for hydrogen production and proved to be an effective and attractive method for converting biomass to energy [10,12]. Gasification is also suitable for large scale hydrogen production [9]. However, until today, all conventional process systems required for hydrogen production is well established in commercial use, except the biomass gasifiers [6,13]. Thus, the development of biomass gasification technology for hydrogen production needs urgent attention.

The process of gasification takes place by converting a feedstock such as biomass into combustible gas mixture, called synthesis gas or syngas, under the controlled conditions of limited amount of oxygen [14,15]. Apart from oxygen, air, steam and their mixtures can be used as the gasifying agent as well. However, gasifying biomass with steam as the gasification agent favors the production of syngas rich in hydrogen [16–21]. In addition, it has been recommended to be the most favorable option for enhancing both hydrogen concentration and yield in the syngas produced [9,22,23]. Nevertheless, biomass steam gasification is inevitably problematic with undesirable CO_2 and tar formed during the process. This may consequently incur a major cost penalty in commercial applications, if separation of hydrogen from hydrogen-rich gas stream contained with impurities, e.g., CO_2, CH_4, CO and tar is needed [16,24]. Thus, if CO_2 and tar produced during steam gasification of biomass can be simultaneously captured and cracked within the process, this technology is likely to be much more attractive and cost-effective in the field of hydrogen production.

Calcium oxide (CaO) has been acknowledged as a catalyst to produce hydrogen-rich gas [19–21,25,26]. Utilization of calcium oxide (CaO) as a CO_2 sorbent in biomass gasification is gaining more interest due to its cheapness and abundance [3,9]. CaO added to the process can play the important roles of not only CO_2 sorbent as mentioned above, but also tar cracking catalyst [9]. This can demonstrate an economically feasible aspect of using CaO to eliminate undesirable CO_2 and tar within the process, instead of the need for expensive and complex downstream cleanup. Nonetheless, the deactivation of CaO after capturing CO_2 can be a challenge in continuous hydrogen production. Frequent refilling of fresh CaO in the process will make the process less attractive economically [27].

To overcome these challenges, the concept of CaO-based chemical looping gasification (CaO-based CLG), which is basically aimed for continuous hydrogen production with in-process CO_2 capture, is thus emerged. Within this looping process, the used CaO can be regenerated and then reused within the cyclic process. Additionally, due to its energy-efficient and environment-friendly aspects, the CaO-based CLG process using biomass fuel, which is gaining more attention in recent years, can play an important role as a promising technology for renewable, sustainable and environment-friendly hydrogen production in near future.

This study first focuses on conventional steam gasification of biomass without catalysts for hydrogen-enriched gas production. A brief review on other technologies for hydrogen production from biomass is also presented to point out why steam gasification of biomass is a promising pathway for sustainable hydrogen production. The effect of process parameters on hydrogen production from steam gasification of biomass is also reviewed. Then the use of CaO in the process to eliminate undesirable CO_2 and tar formation is described. The concept of CaO-based CLG of biomass is discussed as a promising process for renewable, sustainable and environment-friendly hydrogen production.

2. Routes for biomass to hydrogen

The current pathways for hydrogen production from biomass can be classified into biological and thermo-chemical methods [6–9].

In biological methods, the specific processes can be classified as follows: (i) biophotolysis of water using green algae and blue-green algae (cyanobacteria), (ii) photodecomposition, (iii) dark-fermentation, and (iv) hybrid system [28]. All biological processes of hydrogen production basically depend on the use of a hydrogen-producing microorganism. Biophotolysis is the method to use light energy to split water molecules into oxygen and hydrogen ion in the presence of micro-algae or cyanobacteria. An attractive and more favored possibility of using this route is the use of solar radiation to directly split water to produce hydrogen [29]. Among all the processes of biological hydrogen production, photo-fermentation is favored because of its relatively higher hydrogen yields, its ability to utilize wide spectral light and to consume organic substrates derived from various waste sources [30]. Nevertheless, some drawbacks of using this process reported by Kirtay [31] are: (i) high-energy demand for nitrogenase enzyme; (ii) low solar energy conversion efficiency; and (iii) demand for anaerobic photobioreactors covering large areas. Dark-fermentation is a ubiquitous reaction under anoxic conditions. This anaerobic reaction enables the mass production of hydrogen via relatively simple processes from a variety of potentially usable substrates without using light. An important advantage of fermentation is fast degradation of solids and other complex organics found in wastes and agricultural products [32]. However, while fermentation is fast, it is not yet efficient for capturing the energy value of biomass to hydrogen [32]. Moreover, even though the fermentative method has

been demonstrated in laboratory and accepted to be a promising route of biological hydrogen production due to its high rate of hydrogen evolution, yields remain low and it is uncertain whether this technology can be developed to produce high yields of hydrogen and become economically competitive with gasoline or with other alternative hydrogen production routes [32]. Hybrid system is a combination of photodecomposition and dark-fermentation coupled with each other in two subsequent stages to enhance the overall yield of hydrogen [32]. In such a system, the anaerobic fermentation of organic wastes produces intermediates, such as low molecular weight organic acids, which are then converted into hydrogen by photosynthetic bacteria in the second step in a photo-bioreactor. Tao et al. [33] reported that the yield of hydrogen produced by this hybrid system was increased two-fold as compared to that utilizing only dark-fermentation.

Operational processes of thermo-chemical method are fundamentally dependent on the environment of controlled operating parameters in a reactor. The thermo-chemical routes for hydrogen production generally consist of pyrolysis and gasification. Pyrolysis is conversion of biomass to liquid, solid and gaseous fractions by heating the biomass in the absence of air or oxygen at around 500 °C [7]. Although pyrolysis can produce solid, liquid, and gaseous products, most of them are designed only for production of char or liquid hydrocarbons as primary products of interest. However, reforming of these primary products can also generate hydrogen-rich gas but this makes the whole system inefficient [34]. Biomass gasification is the process taking place at high temperature (typically 800 – 900 °C) by partial oxidation to convert biomass into combustible gas mixtures including hydrogen. In general, as compared to pyrolysis, the temperature of gasification is higher and the yield of hydrogen from the gasification is also higher [31].

Among the different technologies for producing hydrogen from biomass, biological methods are found to be less energy-intensive and more environment-friendly compared to thermo-chemical methods [35]. However, low rate of hydrogen production and yield is likely to be a major challenge for biological methods. Due to these constraints, biomass-based hydrogen production using biological methods had so far not been considered as important in most scenarios of future hydrogen economy. Ni et al. [11] analyzed alternative biological and thermo-chemical technologies for biomass-based hydrogen production and concluded that the thermo-chemical hydrogen production routes (pyrolysis and gasification) are economically viable and likely to become competitive with the conventional natural gas reforming method. Biomass gasification has been identified as a possible system for producing renewable hydrogen by developing highly efficient and clean large-scale hydrogen production plants and to lessen dependence on fossil energy sources [6,9,31,36].

Considering the different technologies for hydrogen production from biomass, gasification has been accepted as an economically viable and environment-friendly option as well as a favorable alternative for higher hydrogen yields and large-scale hydrogen production. As a result, this technology is likely to play a major role in the future need of green environment and hydrogen based energy economy.

3. Hydrogen-enriched gas production from biomass gasification

3.1. Mechanism of biomass gasification

Biomass gasification reaction processes generally refer to thermo-chemical conversion of biomass, using a gasification agent, into gaseous products typically including H_2, CO, CH_4, CO_2, H_2O and other gaseous hydrocarbons (CHs). In general, a typical biomass gasification process consists of drying, pyrolysis, combustion and reduction. The mechanistic steps of gasification are explained below and the important reactions are summarized in Table 1.

- Drying: The moisture in the biomass is driven out and converted into vapor. The feedstock in this zone is not decomposed because the temperature is not high enough to cause any chemical reaction.
- Pyrolysis or devolatilization: Dried biomass feedstock from the previous reaction is decomposed into low to high molecular weight volatiles including tar and solid char, as presented in Eq. (1), in the absence of oxygen. The reactions in this zone are endothermic, thus the heat needed for this zone is supplied from the combustion of biomass in the adjacent zone.
- Combustion or oxidation: The products of the pyrolysis reactions are partially oxidized with oxygen contained in the air supplied and then form carbon monoxide, carbon dioxide and water as shown in Eqs. (2)–(4). As combustion reactions are exothermic but other reactions in gasification are endothermic, the overall heat required for endothermic reactions is supplied by this process.
- Gasification or reduction: The chemical reactions in this zone take place in the absence of oxygen because oxygen is consumed in the combustion reactions. The final products from this reaction are mainly gas mixtures including carbon monoxide, carbon dioxide, hydrogen and methane. The formation reactions of these gases take place as shown in Eqs. (5)–(10).

Table 1
Important reactions in biomass gasification.

Name of reaction	Chemical equation (equation no.)	
Pyrolysis	Biomass + heat → gases (H_2 + CO + CO_2 + H_2O + CH_4 + CnHm) + tar + char	(1)
Combustion	$2C + O_2 \rightarrow 2CO$	(2)
	$C + O_2 \rightarrow CO_2$	(3)
	$2H_2 + O_2 \rightarrow 2H_2O$	(4)
Boudouard	$C + CO_2 \rightarrow 2CO$	(5)
Water gas (primary)	$C + H_2O \rightarrow CO + H_2$	(6)
Water gas (secondary)	$C + 2H_2O \rightarrow CO_2 + 2H_2$	(7)
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	(8)
Methanation	$C + 2H_2 \rightarrow CH_4$	(9)
Methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	(10)
Tars reforming	Tars + H_2O → H_2 + CO_2 + CO + hydrocarbons + …	(11)
Hydrocarbon reforming	Hydrocarbons + H_2O → H_2 + CO_2 + CO	(12)

3.2. Types of gasification

In gasification reactions, one of the factors which has significant influence on quantity and quality of the product gas is the gasifying agent. Air, oxygen, steam as well as mixtures of these can be generally utilized as a gasifying agent. The choice of which depends on the desired product gas composition and energy considerations. Air gasification of biomass seems to have a feasible application and has been developed actively for industrial applications. However, this technology produces low calorific value gases of 4 – 6 MJ/Nm^3 and an 8 – 14 vol% H_2 [37,38]. Oxygen gasification could produce a better quality of product gas with medium calorific value, but it needs a pure oxygen supply which may cause simultaneous penalty of cost and safety [10,11,14]. Biomass steam gasification could produce medium calorific value gases (10 – 16 MJ/Nm^3) and especially the product gas rich in hydrogen content (30 – 60 vol%) [38,39].

In the open literature, there are many research works using these kinds of gasifying agents. This study mainly emphasizes the important aspects of the biomass gasification process relevant to hydrogen-enriched gas production.

Zhang et al. [40] conducted an air-blown fluidized-bed gasification experiment aimed to produce product gas rich in hydrogen from seed corn. The experiment resulted in product gas with relatively low concentrations of hydrogen (about 8 vol%). Once steam was supplied, hydrogen content in the product gas increased to almost 30 vol% due to steam reforming of tars and light hydrocarbons and reacting steam with carbon monoxide via the water-gas shift reaction (Eq. (8)). Chang et al. [41] experimentally studied gasification of commercial cellulose and agricultural wastes, i.e., bagasse and mushroom, with air and mixtures of air and steam in a fluidized bed for hydrogen production. They also investigated the influence of varied steam-to-biomass ratio (S/B). When S/B of 0.0 (i.e., no steam or only-air gasification), reaction temperature 800 °C and equivalence ratio (ER) 0.27, hydrogen content was found at 13.5 vol%. Once partial amount of steam was introduced to the same process and operating conditions by varying S/B to 1, hydrogen concentration raised to almost 20 vol%. The effect of using different gasifying agents on hydrogen composition in the product gas is compared in Fig. 1.

Fig. 1 shows the effect of different gasification agents, i.e. air, oxygen and steam, on the hydrogen concentration. Air gasification studies conducted by Mohammed et al. [14], Chang et al. [41], and Salleh et al. [42] are considered here as a meaningful baseline to compare the enhanced concentration of hydrogen produced by introducing both partial [38,43] and pure [44] amount of steam to the gasification process. Moreover, oxygen gasification conducted by Zhou et al. [45] is also compared. Compared to air gasification, using pure oxygen as a gasifying agent could produce the product gas with better calorific value (due to no dilution effect from nitrogen) and hydrogen content. This can be seen from Fig. 1 in which the range of hydrogen content from oxygen gasification is higher than that of air gasification. In case of partial amount of steam diluted in air or oxygen gasification, the resulting product gas is relatively richer in hydrogen composition. On the other hand, in the absence of both air and oxygen, pure steam gasification experiment conducted by Gao et al. [44] showed higher hydrogen concentration.

Gil et al. [23] examined the effect of air, steam-oxygen mixtures and pure steam as gasifying agent. The results of Gil et al. [23] agreed with the previous studies as summarized in Fig. 2. It can be seen that the range of hydrogen content is higher in case of gasifying with pure steam and the next is the gasification with the mixture of steam and oxygen. The phenomenon of higher hydrogen content results from the decomposition of water (in the form of steam) added to the thermo-chemical conversion of biomass. As water-gas reaction (Eq. (6)) and water-gas shift reaction (Eq. (8)) take a key role in the steam gasification process, hydrogen production increased [44]. More detailed parametric study of biomass steam gasification reactions relevant to hydrogen production is discussed in Section 5.

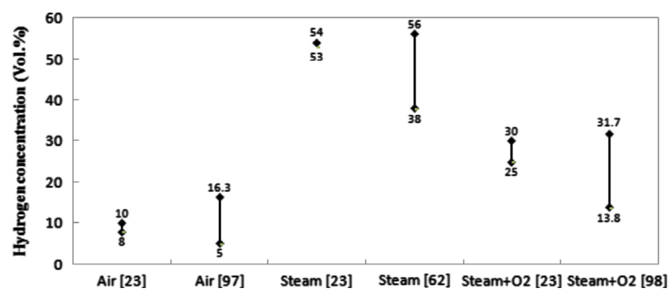


Fig. 2. Comparative study of hydrogen production from different gasifying agents [97,98].

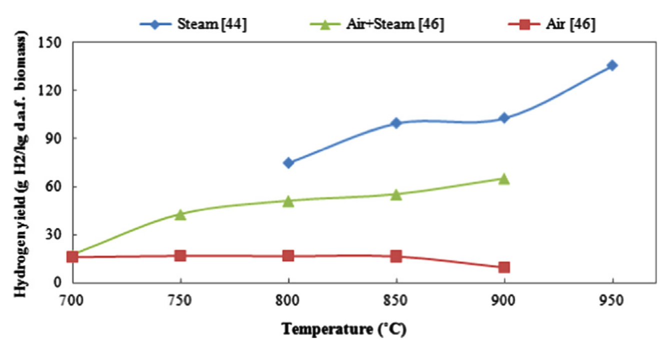


Fig. 3. Effect of using different gasifying agents on hydrogen yield.

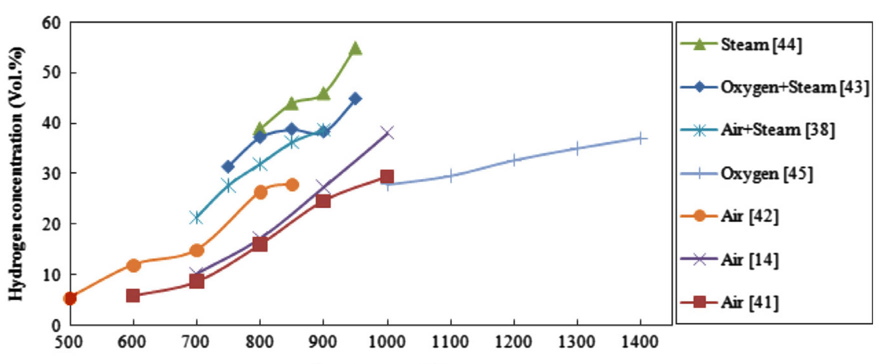


Fig. 1. Effect of using different gasifying agents on hydrogen concentration.

A gasification agent influences not only the quality of product gas but also its quantity. Turn et al. [43] examined the effect of gasifying agents on the amount of hydrogen in the product gas using a bench-scale fluidized-bed gasifier and sawdust with the mixtures of oxygen and steam as a gasifying agent. The resulting hydrogen yield at S/B = 1.7 varied from 62 (at ER of 0.37) to 128 g H_2/kg biomass (at ER of 0.0, i.e., no oxygen or only steam was present). Gonzalez et al. [46] investigated the reactions influencing air and steam/air gasification of biomass (olive oil waste) for production of hydrogen-rich gas. Their experimental works were conducted with three experimental series in the same reactor. First was air gasification and the second was steam/air gasification using steam diluted in air in the first case. The last was catalyzed steam gasification. The different range of hydrogen yield obtained using different gasifying agents is shown in Fig. 3. As compared to air gasification, adding steam to the process helps to enhance the production of hydrogen. The result of hydrogen yields obtained by Gao et al. [44] using pure steam also added to Fig. 3 for comparison.

Nipattummakul et al. [47] produced hydrogen and syngas from sewage sludge via air and steam gasification and found that hydrogen yield increased three-fold in the case of steam gasification as compared to air gasification. Other authors also have reported higher hydrogen yields due to the introduction of steam to gasification process [16,17].

Although a direct comparison of hydrogen concentration and yield due to different gasifying agents is not possible due to variation of many different operating conditions, such as biomass feedstock, reaction temperature, reactor design, equivalence ratio, and steam-to-biomass ratio, the study results compared above provide a general insight into the influence of different gasifying agents. As evidenced in the literature, adding steam to gasification process leads to the production of syngas rich in hydrogen. Especially, pure-steam gasification has a considerable influence on hydrogen composition and yield in the product gas.

4. Hydrogen production costs

One of the problems in the use of hydrogen as a fuel is its unavailability in nature that consequently leads to the need for inexpensive production methods [6]. The production of hydrogen can be achieved by various primary energy sources and different methods, some of which are shown in Table 2 with comparison of related production costs [6].

Table 2 presents an IEA [48]'s long-term scenario of hydrogen production cost from different primary energy sources and technologies. The majority of hydrogen produced today comes from reforming of natural gas and petroleum and coal gasification [49,50]. Hydrogen production using steam methane reforming (SMR) process is the most economical method among the current commercial processes [51]. Rothwell and Williams [52] reported that the cost of hydrogen using natural gas (6 US$/GJ natural gas price) via SMR process is about 12 US$/GJ. However, in fossil based process, capturing CO_2 produced during the process adds about 25–30% to the original cost of hydrogen production [53]. This results in higher cost for hydrogen production from natural gas via SMR process as appeared 12–18 US$/GJ, similar to use of coal reported 13–18 US$/GJ (Table 2). The production of hydrogen from biomass gasification is not expected to develop in the near term due to costs, lack of demonstrated technology, and lack of widespread hydrogen market and infrastructure [6]. However, for long-term view point, it is forecasted to be cost-competitive, if the variability in feedstock prices and the likely use of CO_2 capture and storage (CCS) are considered in the use of fossil fuel based process [54]. This cost-competitiveness with fossil based processes is also evidenced in total cost (14–25 US$/GJ) of hydrogen production from biomass gasification as shown in Table 2. The cost of producing hydrogen from supercritical water gasification of wet biomass was several times higher than that from SMR process [51]. Another alternative method for hydrogen production from biomass is pyrolysis, the hydrogen production cost of which was reported in the range of 8.86–15.52 US$/GJ [55]. Besides biomass gasification, Table 2 also reports the hydrogen production costs from other primary energy sources and technologies but their production costs are still uneconomical, when compared to fossil based processes and biomass gasification. Although biomass gasification is expected to become a cost-effective process, the economies of scale of the process's facilities also have influence on the hydrogen production cost. It was reported that low costs of producing hydrogen are attained with facilities larger than 100 t/day of hydrogen [51].

5. Parametric study

Several operating conditions influence the amount of hydrogen in the product gas from steam gasification of biomass. Influence of the important operating conditions are analyzed and summarized in this section.

5.1. Effect of biomass characteristics

Many researchers carried out gasification of different types of biomass for the production of hydrogen. Florin and Harris [16] have characterized biomass based on: (i) the chemical constituent (cellulose, hemicelluloses and lignin); (ii) elemental composition; (iii) inherent mineral content; (iv) amount of volatile matter; (v) moisture content; and (vi) physical properties (particle size, shape and density). All these parameters have been recognized to influence the product gas composition and yield during biomass steam gasification [19,41,56]. Table 3 shows the characterization of different biomass by Franco et al. [19]. They investigated the effect of different biomass types on the steam gasification process in an

Table 2
Hydrogen production cost for long-term scenario.

Method	Feedstock price	Feedstock cost ($/GJ H_2)	Other prod. cost ($/GJ H_2)	Transport cost ($/GJ H_2)	Refueling cost ($/GJ H_2)	Total cost at fuel pump ($/GJ H_2)
Natural gas with CCS	3–5 $/GJ	3.8–6.3	1.2–2.7	2	5–7	12–18
Coal with CCS	1–2 $/GJ	1.3–2.7	4.7–6.3	2	5–7	13–18
Biomass gasification	2–5 $/GJ	2.9–7.1	5–6	2–5	5–7	14–25
Onshore wind	3–4 cents/kWh	9.8–13.1	5	2–5	5–7	22–30
Offshore wind	4–5.5 cents/kWh	13.1–18.0	5	2–5	5–7	27–37
Solar thermal elec.	6–8 cents/kWh	19.6–26.1	5	2–5	5–7	32–42
Solar PV	12–20 cents/kWh	39.2–65.4	5	2–5	5–7	52–58
Nuclear	2.5–3.5 cents/kWh	8.2–11.4	5	2	5–7	20–27

atmospheric-pressure fluidized-bed gasifier and correlated the product gas composition and yields with the type of biomass species. The nature of biomass species appeared to influence the variations in the gas composition as evidenced from the experimental study of Franco et al. [19] and shown in Fig. 4.

Chang et al. [41] investigated the biomass gasification to produce the hydrogen and syngas in a fluidized bed. They used three different species of biomass (i.e., commercial cellulose, bagasse and mushroom waste) at different reaction temperatures (700 – 900 °C), ER (0.27 – 0.34) and S/B (0 – 0.5). The hydrogen production was found to be highest in case of using commercial cellulose corresponding with its higher carbon-hydrate concentration than the other two species. In addition, for the biomass with relatively high ash contents like mushroom waste, it was noticed that the deposition of ash and char produced in the gasifier may block the manifold which may lead to the lower gas production capacity.

Other examples of the influence of biomass species on the product gas can be seen in Nipattummakul et al. [17], Ahmed and Gupta [57–59], who have studied steam gasification using sewage sludge, paper, food wastes, and plastics, respectively. The comparative results show that syngas and hydrogen evolution from steam gasification of sewage sludge is slower than that of paper, food wastes and plastics. On the other hand sewage sludge yielded more hydrogen than that from paper and food wastes.

Ahmed and Gupta [60] also investigated the characteristic of syngas and hydrogen evolution from pyrolysis and gasification of rubber. Rubber consisting of relatively low hydrogen-to-carbon ratio yielded less hydrogen than wood.

Several authors have studied the effect of biomass particle size on the steam gasification reactions. Rapagná and Latif [61] investigated the influence of biomass particle size and temperature on product yield and distribution using almond shells with steam in a continuous bench-scale fluidized-bed reactor. The mean size of almond shell particle was varied between nearly 300 μm and over 1 mm under the bed temperature ranging from 600 to 800 °C. The experimental result found that the yield of hydrogen and total gas decreased with increasing particle size in the entire range of operating temperature. However, at higher temperature, the influence of smaller particle sizes was practically found no significant differences in product yield and distribution. These results were similar to those obtained by Herguido et al. [62].

Herguido et al. [62] also studied the effect of different types of biomass feedstock on the yields of gas, char and tar as well as the composition and heating value of the product gas. Pine wood

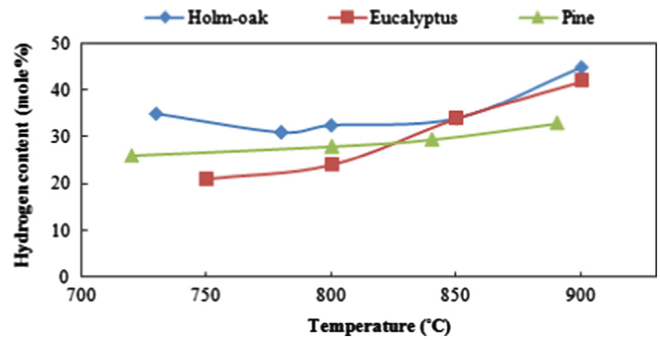


Fig. 4. Hydrogen content derived from steam gasification of different biomass species.

chips, pine sawdust, thistles, and cereal straw were gasified with steam in a fluidized-bed reactor operated at the temperature range of 650 – 780 °C. The differences in size of pine sawdust and pine wood chips influenced total gas yield and composition. The gas yield of 1.2 kg, and 0.7 kg per kg of pine sawdust and kg of pine wood chips obtained, respectively. This shows that the smaller the particle size, the greater the gas yields. Nevertheless, the differences in product yield and distribution resulting from different particle size were not significant when the operating temperature increased to a maximum of 780 °C.

Recently, Luo et al. [63] also studied the effects of biomass particle size at different bed temperatures on product yield and composition. Municipal solid waste (MSW) with different particle size fractions (i.e., below 5 mm, 5 – 10 mm and above 10 mm) was used to investigate the influence of particle size on gasification and pyrolysis performance. The result showed that total gas yield increased with the decreasing particle size at the same temperature. Furthermore, smaller particle sizes allowed higher hydrogen and carbon monoxide and less carbon dioxide contents. The major difference in product yield and composition is due to different particle size practically disappeared at the highest temperatures. The results of Luo et al. [63] strongly agree with the study results of Rapagná and Latif [61] and Herguido et al. [62]. In addition, the similar result is observed from many other studies such as Lv et al. [38] and Luo et al. [56].

It is generally found that smaller particles can produce higher gas yield. Di Blasi [64] reported that higher heating rates produce more light gases as well as less char and condensate. Since smaller particles contribute to a larger surface area and hence faster heating rates, it can be expected that the size of biomass particle has a significant influence on the product gas yield. Moreover, it is generally reported that the smaller particles produce more hydrogen and carbon monoxide and less carbon dioxide contents than the larger ones [56,63]. As mentioned by Lv et al. [38], this result is related to the fact that the fractions of the carbon monoxide, carbon dioxide and hydrogen are linked together by the equilibrium of the water-gas shift reaction (Eq. (8)) under test conditions. Besides, water-gas reaction (Eqs. (6) and (7)) and Boudouard reaction (Eq. (5)) have an important role to contribute these gas species in the initial phase of biomass gasification reaction.

In order to improve the quality and quantity of product gas or even increasing hydrogen and carbon monoxide, minimizing the size of feedstock seems to be an alternative method suitable for the gasification process.

5.2. *Effect of gasifier temperatures*

Since gasification is known as one of the thermo-chemical processes using heat to convert the feedstock into product gas, temperature at which heat is supplied has a major influence on the

Table 3
Analysis of different biomass species [19].

Properties	Pine	Holm-oak	Eucalyptus
Proximate analysis (wt%)			
Volatile	71.5	70.2	74.8
Fixed carbon	16.0	17.8	13.9
Ash	0.5	2.4	0.7
Moisture	12.0	9.5	10.6
Elemental analysis (wt% d.a.f.)			
Carbon	51.6	51.1	52.8
Hydrogen	4.9	5.3	6.4
Nitrogen	0.9	0.9	0.4
Sulfur	Not detected	Not detected	Not detected
Oxygen	42.6	42.7	40.4
HHV (kJ/kg d.a.f.)	20,189	19,448	21,250
Chemical composition (wt%)			
Celluloses	39.4	33.9	43.1
Hemicelluloses	27.8	21.8	28.8
Lignin	32.8	44.3	28.1

reaction and consequently on the amount and composition of the product gas generated. The yield of product gas and hydrogen is subjected to reactor temperature [61]. Furthermore, the relationship between reaction temperature and gas yield has been well studied by many researchers [43,62,65]. Higher gasification temperature produces a product gas rich in H_2 and CO but with small amounts of CH_4 and higher hydrocarbons [7]. Nipattummakul et al. [47] and Shen et al. [66] found that with the increase of reaction temperature, H_2 and CO increased, while CO_2 and CH_4 decreased. Similar trends were observed by Chang et al. [41], Turn et al. [43], Gao et al. [44,67], although there were some differences in operating conditions. The comparison developed in the present study provides a general insight into the influence of reaction temperature on the H_2 output.

Fig. 5 shows the effect of temperature on hydrogen concentration in the product gas produced from biomass steam gasification. The results obtained from all studies have a good agreement with each other, i.e., an upward trend of H_2 content related to elevated temperature. It can be concluded that an increase in reaction temperature tends to enhance the extent of conversion of a biomass fuel to a gas product. The possible explanation supporting this statement can refer to the experimental study of Nipattummakul et al. [17] and Ahmed and Gupta [59] on solid residues influenced by reactor temperature. They reported that the decreasing residual solid leftover after gasification was subjected to an increment of reactor temperature. This indicates a better conversion of biomass into product gas due to higher heating rate resulting from a rise of reactor temperature, which consequently results in higher gas yields and enriched H_2 and CO contents. The increase in gas yields and H_2 as explained by Franco et al. [19] and Gao et al. [44] could be due to various reasons, such as: (i) fast pyrolysis at the commencement of biomass introduced into reactor, (ii) endothermic char gasification reactions, and (iii) steam reforming and cracking of heavier hydrocarbons and tars. Moreover, referred to Le Chatelier's principle, higher temperatures favor the reactants in exothermic reactions and the products in endothermic reactions. Therefore, the endothermic reaction (Boudouard reaction (Eq. (5)), water-gas reaction (Eq. (6)) and steam reforming reaction (Eq. (10))) were strengthened with increasing temperature, which causes an increase of H_2 and CO concentration and a decrease of CH_4 and CO_2 concentration. On the contrary, there have been some studies, such as Franco et al. [19] and Li et al. [68], having the trends of CO and CO_2 opposite to the trends mentioned in earlier studies. The downward and upward trends of CO and CO_2, respectively, are possibly attributed to water-gas shift reaction (Eq. (8)) and higher reaction rate for CO_2 production caused by increasing temperature. The water-gas shift reaction is influenced by the presence of steam favorable for the reaction leading to an increment of H_2 and CO_2 as well as a decrease of CO contents with elevating temperature. More details on the influence of steam on the gasification reaction are provided in Section 5.3.

Besides the effect on gas yield and composition, the variation of reactor temperature also influences the evolution of the hydrogen flow rate and the time of hydrogen release [17,47]. The increase of reactor temperature in the steam gasification process enhances hydrogen flow rate and shortens the time of hydrogen release [17,47]. This is attributed to the endothermicity of hydrogen release for the gasification process and increment in reaction rates with increasing reactor temperature [59]. Ahmed and Gupta [60] also found similar result.

As seen in the literature, the reactor temperature exhibits the dominant experimental parameter, influencing both the amount and concentration of H_2 in the product gas as well as the total gas yield. The favorable range of reactor temperature observed by researchers is between 650 and 1000 °C. Higher reactor temperature affects higher heating rate which leads to a better conversion of biomass into the product gas and consequently allows the gas rich in H_2. Moreover, the enriched H_2 in the product gas is promoted by the endothermic reactions (Boudouard reaction (Eq. (5)), water-gas reaction (Eq. (6)) and steam reforming reaction (Eq. (10))), which are strengthened with the rise of temperature. However, the H_2 derived from steam gasification depends not only on the reaction temperature but also the amount of steam fed to the reactor. The H_2 gas enriched with the presence of steam in the process can be explained by water-gas shift reaction (Eq. (8)). Increasing temperature also influences higher mass flow rate of hydrogen produced and shorter time of hydrogen release.

5.3. Effect of steam-to-biomass ratio

Steam-to-biomass ratio denoted by S/B refers to the feed of steam per the feed of biomass [41]. It could practically be varied either by changing the biomass feed rate while holding the steam flow rate constant or vice versa. The S/B is an important parameter, like temperature having a strong influence on both the yield and concentration of H_2 in the product gas as well as the total gas yield [69].

Many researchers have found that increasing the amount of steam fed to the gasifier leads to a rise of H_2 production. This fact can be evidenced from the study results of Turn et al. [43], Gao et al. [44] and Herguido et al. [62]. Figs. 6 and 7 show tendency of H_2 concentration and yield, respectively, corresponding to higher S/B. The higher production of H_2 due to the influence of steam is probably attributed to water-gas shift reaction (Eq. (8)) and steam reforming reaction (Eq. (10)). Apart from an increase in H_2, the water-gas shift reaction (Eq. (8)) promoted by the greater amount of steam (higher S/B) would be accompanied by an increase in CO_2 concentration in the product gas. These trends have been reported by several researchers [19,38,43,66]. Additionally, the researchers also found that CO concentration decreased with higher S/B, which is the consequent effect of promoted water-gas shift reaction. The undesirable increase in CO_2 concentration is inevitably

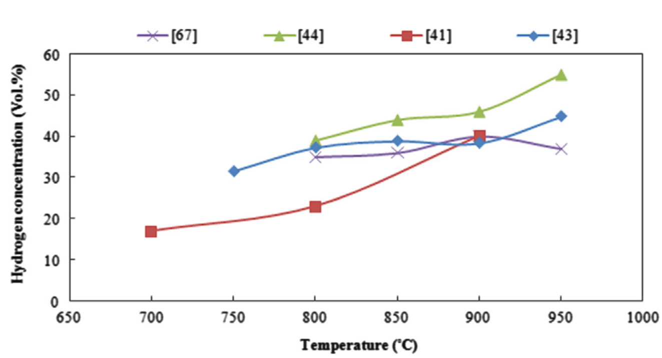


Fig. 5. Effect of temperature on H_2 concentration from biomass steam gasification.

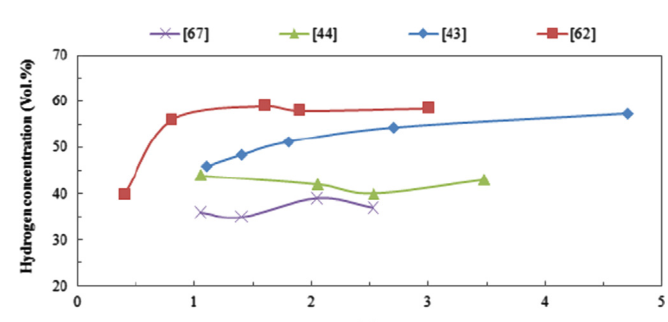


Fig. 6. Effect of S/B on H_2 concentration from biomass steam gasification.

problematic in hydrogen-enriched gas production from conventional biomass steam gasification due to water-gas shift reaction. However, one promising option to eliminate the problem is using CaO-based CO_2 sorbent and this option is discussed in detail in Section 6.2.

Besides the enhancement of H_2 production, increasing S/B has an influence on decreasing char and tar yields [62,67]. This phenomenon is likely attributed to char gasification, steam reforming and tar cracking reactions, which lead to higher conversion as well as higher gas production. Reed [70] stated that the presence of steam enhances participation of tar in steam gasification. This phenomenon results in the decrease in tar content at higher S/B. As a result, the yields of H_2 and total gas can increase as products of tar reforming reaction (Eq. (11)).

In practice, excess steam is often used to drive the cracking and reforming reactions, according to water-gas reaction (Eqs. (6) and (7)). Nevertheless, use of excess steam may cause some disadvantages including high water quantity in the product gas, which consequently leads to more energy consumption in separation of steam out of the product gas via downstream process of condensation and dryness. In addition, the lower yield of H_2 and product gas as well as lower H_2 content with higher S/B due to excess steam fed to the reactor was observed in many studies [12,41,71]. Some obvious cases of excess steam that adversely influences H_2 production are found by Gao et al. [67] in Fig. 6 and Gao et al. [44] in Fig. 7. The trend of H_2 increased first and then declined with continued increase of S/B. The declination is probably attributed to a decrease in temperature of gasification reaction due to the heat absorbed by excess steam. The reduced temperature affected by excess steam can also result in the increase in tar content. Tar formation is one of the major issues that occur during biomass gasification [11]. The unwanted tar may cause the formation of tar aerosols and polymerization to a more complex structure that are not favorable for hydrogen production through steam reforming [11]. Currently, there are several methods to minimize tar formation, such as proper design of gasifier, proper control and operation, and catalysts [11]. In the present study, only the last method is discussed in Section 6.2 focusing on calcium oxide (CaO).

On the other hand, use of insufficient steam may lead to incomplete reaction with the biomass during the gasification process. Consequently, water-gas reaction (Eqs. (6) and (7)), steam reforming reaction (Eq. (10)) and mainly water-gas shift reaction (Eq. (8)) would not appear to reach a state of completion. Therefore, to maximize H_2 production, the optimal S/B should properly be selected according to different operating conditions including biomass characteristics, reactor temperature as well as the type and design of the reactor. The differences in optimal level of S/B have been reported by many authors for H_2 production from biomass steam gasification. Table 4 summarizes the important investigations found in this area. Even though the optimal S/B which has been investigated by several researchers is different from each other, the increasing trend of H_2 output with an increase of S/B up to some extent shows a strong agreement.

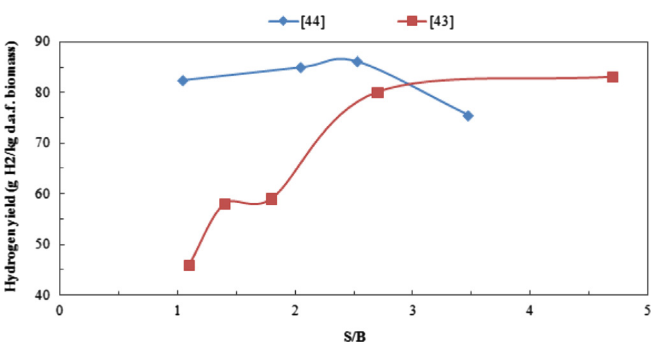


Fig. 7. Effect of S/B on H_2 yield from biomass steam gasification.

Table 4
Summary of important investigations on steam gasification of biomass without catalysts.[a]

Reactor	Biomass	Gasifying agent	Temperature (°C)	S/B	ER	H_2 yield (g/kg d.a.f.)	H_2 content (Vol%)	References	Remarks
Fluidized bed gasifier	Pine, eucalyptus and holm-oak	Steam	700 – 900	0.4 – 0.85	0	N/A	21 – 45 (*Maximum found at gasification of holm-oak at 900 °C, S/B of 0.8 and ER of 0*)	Franco et al. [19]	
Fluidized bed gasifier	Sawdust	Steam and oxygen	750 – 950	1.1 – 4.7	0 – 0.37	23 – 83 (*Maximum found at 800 °C, S/B of 4.7 and ER of 0*)	27.6 – 57.4 (*Maximum found at 800°C, S/B of 4.7 and ER of 0*)	Turn et al. [43]	
Fluidized bed gasifier	α-Cellulose	Steam and air	800	0 – 1.5	0.27	N/A	13.50 – 18.56 (*Maximum found at 800°C, S/B of 1 and ER of 0.27*)	Chang et al. [41]	Values of H_2 yield in the interested range were not reported
Fluidized bed gasifier	Pine sawdust and wood chip, and cereal straw	Steam	650 – 780	0.4 – 3.0	0	N/A	59 (*Maximum found at750°C, S/B of 0.8 and ER of 0*)	Herguido et al. [62]	
Fluidized bed gasifier	Rice hull	Steam	700 – 800	N/A	0	N/A	32.80 – 42.62 (*Maximum found at 800°C, S/B of 5.2 and ER of 0*)	Boateng et al. [96]	
Updraft gasifier	Pine sawdust	Steam and oxygen	850	1.05 – 3.47	0	75.41 – 86.08 (*Maximum found at 850°C, S/B of 2.53 and ER of 0*)	≅ 42 – 43.37 (*Maximum found at 850°C, S/B of 3.47 and ER of 0*)	Gao et al. [44]	Only fixed temperature of 850°C and varied S/B was conducted on steam gasification without catalyst.
Updraft gasifier	Pine sawdust	Steam	800 – 950	1.05 – 2.53	0	39.03 – 79.91 (*Maximum found at 950°C, S/B of 1.4 and ER of 0*)	≅ 34.5 – 41 (*Maximum found at 850°C, S/B of 1.4 and ER of 0*)	Gao et al. [67]	

[a] Compiled from previous experimental study of steam gasification of biomass without catalysts.

5.4. Effect of equivalence ratio

The equivalence ratio (ER) is another important factor in the biomass steam gasification when the air or oxygen is partially used to mix with steam as a gasifying agent in the processes. However, since the presence of nitrogen in the air dilutes the product gas and decreases the gas quality, oxygen has been introduced as a gasifying agent in many cases. ER is defined as the ratio of the amount of air supplied relative to the amount of air needed for stoichiometric combustion [44,72]. The variation of ER means the change in the amount of oxygen introduced into the gasifier, which affects the gasification temperature and reactions and finally influences the product gas quality. It has been reported by several authors that there exist two contradictory effects of ER [38,72]. On one hand, higher ER would cause a degradation of gas quality because more combustible gases including H_2 are consumed due to more oxidization reactions. On the other hand, higher ER could lead to a higher gasification temperature, which can accelerate the gasification and improve the product gas quality to some extent. The effect of ER on hydrogen production has been reported in literatures extensively [43,44,73].

Figs. 8 and 9 present the effect of ER on hydrogen concentration and yield respectively in the product gas produced from biomass steam gasification. From both figures, the experimental result of Lv et al. [73] shows a good agreement with the theory of two contradictory effects of ER. ER was varied in the range of 0.22 – 0.3 with fixing the oxygen flow rate at 1.5 Nm^3/h and S/B at 0.17, and varying the feeding rate to explore the impact of ER on hydrogen production from downdraft gasifier. Change of ER resulted in the variation of temperature in oxidation zone from 798 to 905 °C, which led to a variation in oxidation reactions. The test result can be explained based on two contradictory effects of ER by dividing the phenomenon into two stages, upward and downward trends of H_2 output with increasing ER. In the first stage, the positive effect of ER played a more important role, so that the H_2 output increased to some extent. In the second stage with still continuously increasing ER, the H_2 output appeared a decreasing trend because oxidation reaction became more important than steam gasification reaction due to the increased oxygen quantity. As a result, more combustible gases including H_2 were consumed to produce more CO_2 and H_2O. Turn et al. [43] carried out experiment in fluidized-bed gasifier with fixing the temperature and S/B at 850 °C and 1.7 respectively and varying ER from 0 to 0.37 at a constant feed rate. Gao et al. [44] tested on updraft fixed-bed gasifier by varying ER in the range of 0 – 0.3 with steady temperature and S/B at 850 °C and 1.4, respectively. However, the test results of both researches have a good agreement on H_2 production related to varying ER as displayed in Figs. 8 and 9. Hydrogen concentration and yield tend to decrease while increasing ER. But, their highest values over the range of varied ER are found when ER is zero. This is because of when oxygen was not introduced into reactor (ER = 0) and only steam as a gasification agent, the reactions of water gas (Eq. (6)) and water-gas shift (Eq. (8)) would play an important role as primary reactions in the gasification process. Nevertheless, once oxygen is added to the reactor (ER increased), the oxidation reactions (Eqs. (2)–(4)) would take part in the gasification process. This also results in more H_2 consumed in the oxidation reaction, which leads to a declination of H_2 produced.

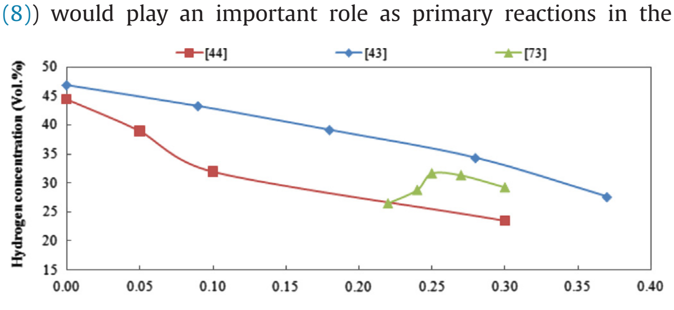


Fig. 8. Effect of ER on H_2 concentration from biomass steam gasification.

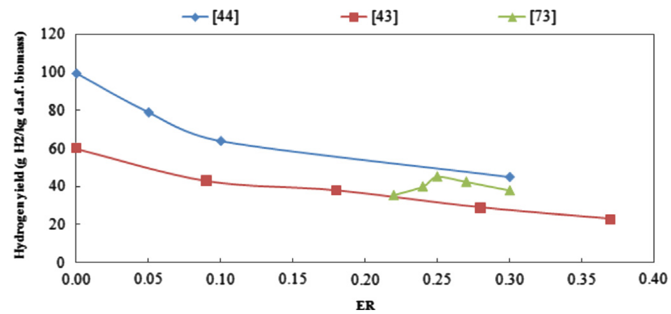


Fig. 9. Effect of ER on H_2 yield from biomass steam gasification.

Overall, ER has complex effects on test results. Through the analysis on the experimental data of varying ER, it can be understood that it is unfeasible to apply too low or too high ER in biomass air-steam gasification. Too low ER will lower reaction temperature, which is unfavorable for biomass air-steam gasification for hydrogen production. Conversely, too high ER will enhance more oxidation reactions, which then consume more H_2 and other combustible gases. So, there exists an optimal value for ER, which varies according to different operating parameters.

6. Challenges and prospects

6.1. Problematic CO_2 and tar production

Even though steam gasification of biomass has been perceived as the attractive pathway for sustainable hydrogen production, the process is inevitably problematic with undesirable CO_2 generation due to water-gas shift reaction. Another serious issue in developing hydrogen production from this process is the formation of unwanted tar which may restrict the quick and widespread use of hydrogen [9]. Tars defined as condensable organic compounds could be produced during gasification and become entrained in the syngas [74,75]. Use of the syngas contaminated with tars can cause fouling and blocking of downstream pipelines and equipments as tars can condense at reduced temperature of the gas. Most post gasification applications therefore require removal of tars to some extent using various techniques before applying the gas [76].

6.2. CaO-based in situ CO_2 and tar reduction

With respect to commercial applications, separating hydrogen from hydrogen-rich gas stream contained with impurities, e.g., CO_2, CH_4, CO and tar incurs a major cost penalty [16,24]. Thus, if CO_2 and tar produced during steam gasification of biomass can be simultaneously captured and cracked within the process, this can be more attractive and cost-effective in the field of hydrogen production. In order to achieve this, some catalysts have been used either inside of the gasifier (called the primary method) or downstream (called the secondary method) [9,77]. Although the latter has been proven to be effective, treatments inside the gasifier as the former one are gaining much attention as these may eliminate the need for complex downstream cleanup [78]. Acknowledged as a catalyst to produce hydrogen-rich gas [19–21,25,26], use of CaO as a CO_2 sorbent in biomass gasification for hydrogen production has currently gained a broad attention due to its cheapness and abundance [3,9,16]. The introduced CaO can play

the vital roles of not only CO_2 sorbent, but also tar cracking catalyst and bed material based heat carrier in a fluidized-bed reactor [9]. Removing CO_2 from the gasification reaction as soon as it is formed alters the equilibrium composition of the produced gas and promotes the production of gas rich in hydrogen [3]. Similarly, the catalytic reforming of tar not only reduces the tar amount in the product gas but also enhances the yields of total gas and hydrogen as well as conversion efficiency [1,36]. Hence, in order to enhance hydrogen production with in-process CO_2 capture and tar reduction, the concept of steam gasification of biomass in the presence of CaO can play an important role as a promising option for sustainable hydrogen production.

Many researchers have recently paid attention to the role of CaO in capturing CO_2 only. Table 5 summarizes the important investigations on the role of CaO as a CO_2 sorbent and tar reforming catalyst [12,79–83]. Fundamentally, CO_2 produced during steam gasification in the presence of CaO would be captured by CaO via a carbonation reaction (Eq. (13)) and then form calcium carbonate ($CaCO_3$). As a result, this reduces CO_2 partial pressure in water-gas shift reaction (Eq. (8)) and then enhances the reaction to move in forward direction to produce more H_2 [9,12,82]. However, the capability of the reaction also depends on other operating conditions, such as S/B, temperature, pressure and CaO content, details of which are described by Florin and Harris [16].

$$\text{Carbonation}: \quad CaO + CO_2 \rightarrow CaCO_3 \tag{13}$$

$$\text{Calcination}: \quad CaCO_3 \rightarrow CaO + CO_2 \tag{14}$$

Besides CO_2 capture, the introduced CaO could also reform tars produced during the gasification process and form gaseous products which result in higher yields of total gas and H_2. This phenomenon could be explained by tar reforming reaction (Eq. (11)) and hydrocarbon reforming reaction (Eq. (12)). Some previous studies in this field are also included in Table 5 [9,26,56,84–87]. Typically, more information in the literature has been focused on total tar mass production. Studying only tar content or tar yield is not enough to fully describe the tar problem [23,88]. In downstream processes, only some specific tar

Table 5
Summary of important investigations on the role of CaO as a CO_2 sorbent and tar reforming catalyst.

Reactor	Biomass	Gasifying agent	Temp. (°C)	S/B	CaO	CaO/B	Tar study*	Gas concentration (Vol%)				References
								H_2	CO_2	CH_4	CO	
Fixed bed	Sawdust	Steam	670	0.83	Calcined limestone	2	N/A	54.43	1.56	21.58	21.92	Acharya et al. [12]
Bubbling fluidized bed	Sawdust	Steam	580	1.5	Calcined limestone	1	N/A	71	1	21	7	Acharya et al. [79]
Fixed bed	Japanese oak	Steam	700	N/A	N/A	2	N/A	880 ml/g	390 ml/g	180 ml/g	N/A	Hanaoka et al. [80]
Fixed bed	Pine sawdust	Steam	800	0.42	Calcined limestone	20	N/A	72 mol%	10 mol%	9 mol%	9 mol%	Wei et al. [81]
Quartz tube	Pine sawdust	Steam	650	0.9	$Ca(OH)_2$ powder	0.5	N/A	57	6	14	23	Guoxin and Hao [82]
Fixed bed	Six energy crops in Poland	Steam	650	N/A	Calcined limestone	4.0–4.7	N/A	73–78	N/A	N/A	N/A	Howaniec and Smolinski [83]
Bubbling fluidized bed	Sawdust	Steam	740	2.18	CaO reagent	1	Tar was studied considering the color change of the condensed tar sample. The color turned from deep red in the absence of CaO into light yellow at CaO/C of 1.	62	9	11	16	Han et al. [9]
Bubbling fluidized bed	Larch	Steam	650	N/A	Calcined limestone	In-bed CaO	Total tar yield was found 31.24 wt% of carbon distribution.	63.56	24.75	5.75	4.85	Weerachanchai et al. [26]
Fixed bed	Pine sawdust (< 0.075 mm)	Steam	900	1.2	Calcined dolomite	N/A	Tar amount was not found at this operating condition.	52	14	6	23	Luo et al. [56]
Bubbling fluidized bed	Crushed almond shells	Steam	770	1	Calcined dolomite	In-bed CaO	The tar content of 0.6, 43 and 2.4 g/Nm^3 was obtained from the experimental tests with CaO, sand and olivine, respectively.	55.5	14.1	6.4	24	Rapagná et al. [84]
Fixed bed	Pine sawdust	Steam	900	2.1	Calcined dolomite	N/A	Tar amount was not found at this operating condition.	52.7	23.9	2.7	17.2	Luo et al. [85]
Fixed bed	Pine bark	Steam	600	N/A	CaO reagent	1	Tar was studied considering particulates and suspended matter. The sample from the gasification without CaO had more particulates and suspended matter as compared to the one with CaO.	83	9.2	1.5	6.3	Mahishi and Goswami [86]
Dual fluidized bed	Wood chips	Steam	675	N/A	Calcined limestone		Tar content was found about 1 g/Nm^3.	50.6	12.3	12.9	16.5	Koppatz et al. [87]

* Tar studies reported in this table were focused only on total tar mass formation.

compounds may be problematic and others may be harmless or even beneficial [89]. Thus, addressing the relation between tar concentration and composition and gasification conditions in a systematic way is fundamental to the efficient operation of commercial biomass gasification systems [74]. This kind of study related to the influence of CaO is still lacking in the literature. The information available in this regard is summarized below.

Pfeifer et al. [90] studied in situ CO_2 absorption in a dual fluidized bed biomass steam gasifier to produce a hydrogen-rich syngas. The results obtained from the Adsorption Enhanced Reforming (AER) process using CaO as a bed material in their study were compared to those obtained from the conventional process without CaO. The former process allowed higher H_2 production of 75 vol%, compared to the latter case which produced only 40 vol% of H_2 in product gas. Tar content as low as 0.5 g/Nm^3 obtained from CaO-based process at 600–700 °C is less than that of 2–5 g/Nm^3 obtained from the process without CaO at 850 °C. This can be implied that no significant increase in tar formation occurs in the process with CaO despite the low gasification temperatures. This consequently results in higher efficiency of energy conversion without compromising the hydrogen-rich gas production and tar reduction. Apart from tar content, tar composition was also studied but it was reported as the influence of solid circulation rate, which could not point out the effect of CaO being focused in this section.

Pfeifer et al. [91] studied the influence of CaO on gas and tar production in the same experimental unit as the one used by earlier workers [90]. The concentration of H_2 and CO_2 in the product gas was 74 vol% and 6 vol% respectively in CaO-based process. Meanwhile, 40 vol% of H_2 and 18 vol% of CO_2 were obtained from the process without CaO. Tar content of 1.4 g/Nm^3 was obtained from CaO-based process at 645 °C, whereas that of 3.53 g/Nm^3 was found in the case without CaO at 841 °C. Despite the significant lower gasification temperature, much lower tar content in the CaO based experiments have been contributed to the higher catalytic activity of CaO on cracking the tar. This catalytic effect could be also noticed from the change in tar composition. It was found that heavier tars in polycyclic aromatic hydrocarbon (PAH) group were catalytically reformed to lighter tar compounds like phenol and styrene in the presence of CaO, as compared to the process without CaO. Similar effect of CaO on tar composition was observed by Jordan and Akay [75].

Jordan and Akay [75] studied the impact of CaO on tar concentration and composition as well as syngas yield by mixing CaO at 2, 3 and 6 wt% with bagasse pellets and then feeding into an air-blown downdraft gasifier. As compared to the baseline case without using CaO, the use of 2, 3 and 6 wt% in-bed CaO promoted the conversion of Class 1, 4 and 5 tars (higher ring tar species) to Class 3 tars (1 ring tar species), which consequently resulted in a decrease in tar yield ranging 16–35%, a decrease in tar concentration of 44–80%, and an increase in syngas yield of 17–37%. As a result of a reduction in higher ring tar compounds in the presence of CaO, tar dew point decreased in the range of 37–60 °C, as compared to the baseline case without CaO. Knowing the tar dew point of the product gas is very useful in commercial applications, as it helps determine the operating conditions of such a system to avoid undesirable tar condensation and deposition due to reduced temperature of the product gas. Besides, it can facilitate an evaluation of the potential impact on downstream equipment. However, the knowledge in this area is still limited in the literature.

6.3. CaO-based chemical looping gasification

From the previous experimental studies summarized in Tables 5 and 6, one can find that the major disadvantage of those processes is a discontinuous hydrogen production due to the deactivation of used CO_2 sorbent. Despite attractiveness in its combined roles as a CO_2 sorbent and tar reforming catalyst, use of CaO may not be economically viable, if fresh CaO is frequently needed to refill to the process after capturing CO_2 via carbonation reaction and then the used CaO in the form of calcium carbonate ($CaCO_3$) cannot be reused in the gasification system. This makes the process less attractive from an economical perspective [92]. To overcome such a challenge, the concept of chemical looping gasification (CLG), which is fundamentally aimed for continuous hydrogen production with in situ CO_2 capture using fluidized-bed technology, is thus emerged. Within this looping system, the used CaO can be regenerated and then reused within the cyclic process between two major reactors, i.e., the regenerator and the gasifier.

Chemical looping is one of several emerging technology options that can facilitate the uptake of low-emission energy technologies and help in a diverse range of applications for productions of fuels, chemicals and electricity [93]. The concept of chemical looping has been found in various applications, such as chemical looping gasification, chemical looping reforming, chemical looping combustion, sorbent chemical looping for post combustion capture of CO_2 and chemical looping air separation. These applications of chemical looping concept have different purpose of main production, details of which are well discussed by Moghtaderi [93]. However, as the present work is focusing on hydrogen production with in situ CO_2 capture, thus only the concept and the past applications and development of CaO-based chemical looping gasification are discussed here.

The applications of the CaO-based chemical looping gasification (CaO-based CLG) process can be traced to early times. The processes for CaO-based CLG include the CO_2 Acceptor Process that was developed in the 1970 s and ended in 1977 after being tested successfully in a pilot plant and proved technically feasible [94]. This is a notable application and forms the basis of recent development in CaO-based CLG processes [94]. Other CaO-based CLG processes that are being developed or have currently been developed include the HyPr-Ring Process, the Zero Emission Coal Alliance (ZECA) Process, the ALSTOM Hybrid Combustion-Gasification Process, and the Fuel-Flexible Advanced Gasification-Combustion (AGC) Process [94]. Some important information of these processes is summarized in Table 6, details of which are however described by Fan [94].

From Table 6, one can see that all CaO-based CLG processes are mainly aimed to produce the product gas rich in hydrogen with

Table 6
CaO-based chemical looping gasification.

Parameters	CO_2 acceptor	HyPr-Ring	ZECA	ALSTOM	AGC
Product	CH_4 and flue gas	H_2 and CO_2	H_2 and CO_2	H_2 , N_2 and CO_2	H_2 , hot air and CO_2
CO_2 capture	No	Yes	Yes	Yes	Yes
Gasifier operating condition	800–850 °C, 10 atm	650 °C, 30 atm	–	880–980 °C, 6 atm	750–850 °C, 17–20 atm
H_2%	65.6%	76%	–	–	80%
Fuel	Coal	Coal	Coal	Coal	Coal
Reactor type	Fluidized bed	Pressurized reactors	Pressurized reactors	Fast fluidized bed	Fluidized bed

integrated CO_2 capture, except only CO_2 Acceptor process. However, these processes are not considered as sustainable and environmental hydrogen production due to the dependence on fossil fuel. Moreover, the processes were designed to operate at high pressure and/or temperature and some of them were complexly designed with multiple-loop configuration for the looping system. These aspects possibly cause high operational complexity and cost as well as high capital cost. Due to these troublesome issues, the current status of the CaO-based CLG is still in the R&D stage, with no commercial plants in operation [93].

To overcome these challenges, the recent researches and developments simplify the configuration of looping system with the single-loop and atmospheric operation. More sustainable and environmental concerns are taken in to account with utilization of biomass feedstock. Fig. 10 presents the schematic principle of recent CaO-basd CLG. This looping system mainly consists of two reactors, i.e., the regenerator and the gasifier. In the gasifier, the biomass fuel is gasified in the presence of CaO and steam to produce hydrogen-rich gas, whereas CO_2 generated during the gasification is instantaneously captured by CaO and then forms $CaCO_3$ via a carbonation reaction (Eq. (13)). Afterwards, the used CaO particles in the form of $CaCO_3$ are circulated to the regenerator to get calcined and then release a highly concentrated stream of CO_2 via a calcination reaction (Eq. (14)). The hot CaO regenerated in the regenerator is then cycled back to the gasifier as a repeated process and also provides additional heat for the gasification process. In addition, heat released by the exothermic carbonation reactions would compensate for the endothermic gasification reactions [79]. Due to these energy-efficient and environment-friendly aspects, a CaO-based CLG process is gaining more interest for sustainable hydrogen production with in situ CO_2 capture in recent years.

With this concept of CaO-based CLG, Acharya et al. [79] developed a single-loop process for atmospheric biomass steam gasification for hydrogen-enriched gas production with in-process CO_2 capture using calcined limestone as a CO_2 sorbent. This single-loop configuration is much simpler than previous CaO-based CLG units, where two or more loops are used. The main components in the process consist of a bubbling fluidized-bed gasifier, a circulating fluidized-bed regenerator, and a cyclone. In theoretical analysis of the process, it was reported that the system efficiency as high as 87.49% can be received at an ideal scenario with 100% CO_2 capture. A volumetric concentration of 71% for H_2 and nearly 0% for CO_2 in the product gas was received from the experiment conducted in a batch-type fluidized-bed gasifier.

Moghtaderi [95] also adopted this single-loop CaO-based CLG concept to produce high-purity combustible gases (e.g., hydrogen) from carbon-based fuel including biomass. Similar to Acharya et al. [79], Moghtaderi [95] found that using CaO from naturally occurring CaO-based material like calcined rocks (limestone or dolomite) suffers from particle attrition (due to weak mechanical strength) and deactivation. This results in greater demands for fresh CaO-based sorbent that would consequently lead to higher operational costs. To avoid these problems, concrete and demolition waste (CDW) was used as a CO_2 sorbent in the looping process. The experimental result shows that the bed of CDW exhibits a very similar behavior to limestone to allow high H_2 and low CO_2 in the product gas. In addition, it was reported that CDW particles do not suffer from attrition issues and are not severely eroded with a repeated number of carbonation–calcination cycles, unlike calcined limestone used by Acharya et al. [79]. Due to these advantages, CDW can also be an option for further research.

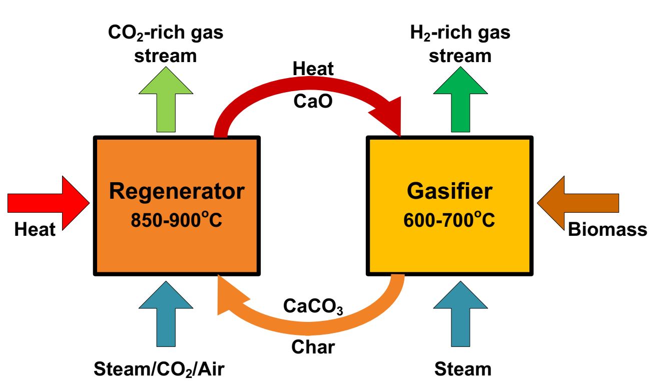


Fig. 10. Schematic principle of CaO-based chemical looping gasification.

Similar to CaO-based CLG concept, an Absorption Enhanced Reforming (AER) process, operated in a dual fluidized bed gasifier (DFBG) has been developed at the Vienna University of Technology with the aim for hydrogen-rich gas production with in situ CO_2 capture. The operational principle of the AER process can be explained with the same Fig. 10 as that of CaO-based CLG detailed earlier. However, there is one major difference applied to a regeneration reactor, details of which are further described below. The experimental investigations in this AER process were conducted by Pfeifer et al. [90,91]. Some important details on the influence of the process on H_2 production, tar reduction and CO_2 capture are previously discussed in Section 6.2. In addition, another test investigation on the same AER setup conducted by Koppatz et al. [87] is also summarized in Table 5.

In contradiction to the CaO-based CLG developed by Acharya et al. [79], the AER process developed at the Vienna University of Technology used direct burning of fuel (residual char circulated with bed material from the gasifier) in the regeneration reactor (so called combustor) rather than using external heaters. This renders the process more energy-efficient. However, since air supplied for combustion causes a production of flue gas (mainly containing N_2 and CO_2), a complex and expensive post-combustion separation system may be required, if one wishes to capture CO_2. To avoid this concern, Acharya et al. [79] later developed the CaO-based CLG, as described earlier, using CO_2 or steam as a regeneration medium in the regenerator heated using external heaters. In this process, pure CO_2 stream was produced from calcination reaction in the regenerator. The production of pure CO_2 stream eliminates the need for downstream CO_2 separation system which consequently lowers operational complexity and cost as well as capital plant cost. Moreover, CO_2 stream produced from calcination reaction can be partially returned to use as a regeneration medium in the regenerator. Nonetheless, the major disadvantage of this process is energy-intensive due to externally heating the regenerator. Both the described processes have different merits. Selection should be balanced with the main purpose of application and the consideration of energy/exergy efficiency and economic feasibility study of the processes. Further research is encouraged as the knowledge in this area remains scarce.

7. Conclusions and recommendations

This work first focuses on conventional steam gasification of biomass without catalysts for hydrogen-enriched gas production. The obvious challenge of undesirable CO_2 and tar formation during the process can be overcome by adding CaO to the process without compromising hydrogen production. The deactivation of CaO after carbonation reaction is also challenging for continuous hydrogen production and long-term stability of the gasification process, which consequently makes the process less attractive both in technical and economical perspectives. Due to these challenges, the concept of CaO-based chemical looping gasification (CaO-based CLG), which is principally aimed for continuous hydrogen

production with in situ CO_2 capture, is thus emerged and gaining more attention in recent years.

Important conclusions drawn from the present study are as follows:

- Several aspects of biomass characteristics have significant influence on hydrogen production. Biomass containing higher cellulose and hydrogen-to-carbon ratio is found to influence higher hydrogen production. Smaller biomass particles which contribute to a larger surface area and hence faster heating rates can allow higher hydrogen production in biomass steam gasification.
- The increase of gasification temperature favors the hydrogen production because higher reaction temperature allows higher heating rate which improves the conversion of biomass into the product gas and consequently provides the gas rich in hydrogen. Increasing temperature also enhances hydrogen flow rate and shortens the time of hydrogen release.
- Increasing steam-to-biomass (S/B) ratio increases the concentration and yield of hydrogen in the product gas since the influence of steam affects the chemical reaction of steam reforming and water-gas shift reactions. However, too much steam can also adversely cause temperature drop in the gasifier, which leads to lower hydrogen production and higher tar formation.
- The variation of equivalence ratio (ER) affects the change in gasification temperature and reactions. Applying higher ER can cause a reduction of hydrogen in product gas due to more oxidation reactions which consume more combustible gases. Conversely, higher ER can also improve hydrogen production since higher gasification temperature driven by higher ER can enhance the gasification reactions and consequently improve the product gas quality.
- One of the challenges for hydrogen production from conventional biomass steam gasification without catalysts is undesirable formation of CO_2 and tar. Use of CaO in the process can absorb CO_2 and lower its partial pressure, therefore moving water-gas shift reaction in forward direction to enhance hydrogen output. Besides, CaO can simultaneously play the role of reforming tar into gas, which consequently results in lower tar content and higher yield of hydrogen and total gas. CaO can catalytically reform tar compounds from higher ring species in polycyclic aromatic hydrocarbon (PAH) group to fewer ring species. Moreover, shifting the tar compounds from heavier PAHs to the lighter species also results in reduction of tar dew point.
- The biggest challenge of using CaO in biomass steam gasification that makes the process less attractive is the deactivation of CaO after carbonation reaction. This directly interrupts continuous hydrogen production and may not be economically viable, if fresh CaO is frequently needed to refill to the process. Use of CaO-based CLG can thus overcome such a challenge and allow continuous hydrogen production with in situ CO_2 capture.
- Based on previous studies discussed in the present work, the following suggestions for future studies and developments to move the present technology towards the commercial use of sustainable hydrogen production from biomass steam gasification are made:
- Use of CaO in the process for hydrogen-rich gas production with in situ CO_2 capture and tar reforming is recommended. In-depth study on tar reforming is encouraged to analyze the effect of CaO on tar compounds. Knowledge of tar compounds can link to tar dew point which is the important indicator that can help to determine the operating conditions of gasification as well as its downstream systems to avoid undesirable tar condensation and deposition due to reduced temperature of the product gas. The information in this area remains limited in literature.
- More development of the CaO-based CLG system is encouraged, as the process is very useful for continuous hydrogen production with in situ CO_2 capture. Optimization study on this process is also needed as this knowledge is still lacking in the literature. Comparative study on different CaO-based bed material can be an option for further research.

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